

Micro-XRF Study of Arsenate Incorporation Into Calcite.

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Beamline: X26A

Introduction: Many studies have demonstrated that significant site selectivity in trace element incorporation takes place during calcite crystal growth. Factors such as charge and ionic size of the impurity introduced and the crystallographic orientation of the calcite surface sites play a major role in this process. The calcite ($10\bar{1}4$) growth surface characteristically exhibits two pairs of vicinal faces denoted as “+” and “-” respectively. These result from the spiral growth mechanism of this surface and reflect differences in growth step orientation, governed by the anisotropy of the calcite structure [1,2] along this plane. Structural difference in growth steps make the + vicinal faces non-equivalent to the - faces (Figure 1). Studies involving other tetrahedral anions, such as SO_4^{2-} , SeO_4^{2-} , BO_4^- [3, 4], have shown that selective incorporation occurs at non-equivalent steps of the calcite ($10\bar{1}4$) face. Our study determined if arsenate (AsO_4^{3-}), a tetrahedral anion, also exhibits selective incorporation at the calcite ($10\bar{1}4$) face.

Methods and Materials: Single calcite crystals were grown from aqueous solution at room temperature. During crystal growth, dissolved $\text{Na}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ was introduced to the system. After 12 hours of exposure, calcite crystals were harvested. Crystals ranging from a 300 to 400 μm were mounted and sectioned for elemental mapping at beamline X26A. Monochromatic radiation (16.5 keV) was used and fluorescence maps were taken across non-equivalent vicinal faces, using a beam size of 10 μm .

Results: In all samples, the - vicinal faces are distinctively enriched in arsenate in comparison to the + vicinal faces of the ($10\bar{1}4$) crystal plane (Figure 2). For a sample reacted with 5 μM arsenate, average As(V) concentrations in the + and - faces are 78 ppm and 144 ppm, respectively. For a sample of 30 μM , average concentrations of + and - are 214 ppm and 299 ppm, respectively. The interaction of arsenate with the calcite surface leads to the formation of macrosteps preferentially on the - vicinal faces; the macrosteps increase in density as the concentration of arsenate increases.

These results show that AsO_4^{3-} is similar to BO_4^- in that these anions prefer the - vicinal faces, whereas SO_4^{2-} and SeO_4^{2-} , are preferentially incorporated [3] into the + faces. Results imply that bulk partition coefficients for As(V) depend on the availability of different calcite surface sites. **References:**

[1] Paquette J. and Reeder R.J. (1995) *Geochim Cosmochim Acta* **59**, 735-749.

[2] Paquette J. and Reeder R.J. (1990) *Geology* **18**, 1244-1247

[3] Staudt W.J., Reeder R.J., Schoonen M.A.A., *Geochim Cosmochim Acta* **58**, 2087-2098

[4] Hemming N.G., Reeder R.J., Hart S.R., *Geochim Cosmochim Acta* **62**, 2915-2922



Figure 1. DIC image of calcite ($10\bar{1}4$) crystal plane showing the pairs of non-equivalent + and - vicinal faces.

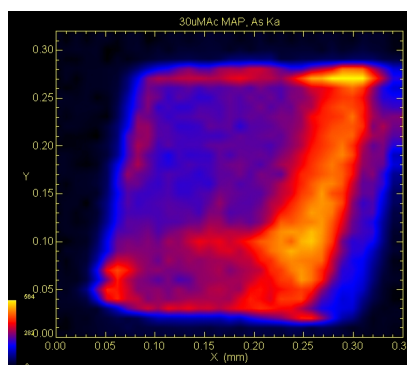


Figure 2. Micro-XRF elemental map showing the preferential incorporation of arsenate on - vicinal faces.